- 1. Magnesium sulfite; MgSO₃; [7757-88-2]
- 2. Water; H₂O; [7732-18-5]

EVALUATOR:

H.D. Lutz, Dept. of Chemistry, University of Siegen, FR Germany. January 1985.

CRITICAL EVALUATION:

Magnesium sulfite crystallizes from aqueous solutions in the form of the hexahydrate, MgSO $_3$.6H $_2$ O [13446-29-2], at temperatures below 313 K and as the trihydrate, MgSO $_3$.3H $_2$ O [19086-20-5], above 313 K (1-4). Furthermore the hydrates MgSO $_3$.3.5H $_2$ O [85017-92-1] (5), MgSO $_3$.2.5H $_2$ O [85017-92-1] (6), MgSO $_3$.2H $_2$ O [40854-09-9] (2,6,7), MgSO $_3$.1H $_2$ O [72860-77-6] (6,7), MgSO $_3$.xH $_2$ O (8), and MgSO $_3$.x'H $_2$ O (8) have been reported. The existence of the hydrate MgSO $_3$.3.5H $_2$ O (5) could not be confirmed (6). It is unknown whether MgSO $_3$.xH $_2$ O and MgSO $_3$.x'H $_2$ O are identical with MgSO $_3$.2.5H $_2$ O or MgSO $_3$.2H $_2$ O, respectively. Solubility data of magnesium sulfite are available for the systems MgSO $_3$ -H $_2$ O, MgSO $_3$ -SO $_2$ -H $_2$ O, MgSO $_3$ -MgSO $_3$ -Mg

SOLUBILITY OF MAGNESIUM SULFITE IN PURE WATER

$MgSO_3.6H_2O$

Numerical data on the solubility of MgSO $_3$.6H $_2$ O in water have been given by several authors (1,8-15). The published data are in relatively good agreement. For ambient temperature the following saturation concentrations have been reported: 0.046 (14) and 0.0573 (15) mol kg $^{-1}$ (molality scale) at 298.2 and 303.2 K respectively, and 0.058 (9) and 0.0501 (10) mol dm $^{-3}$ (molarity scale) at 298 and 291 K, respectively. The most reliable solubility data seem to be those of Trendafelov et al. (14) and Nývlt et al. (15).

RECOMMENDED VALUES

The solubility of MgSO $_3$.6H $_2$ O in water at 298.2 K (25°C) on the molality scale is 0.050 ($^{\pm}$ 0.005) mol kg $^{-1}$ (5.2 g MgSO $_3$ /kg H $_2$ O).

The solubility of $MgSO_3$.6 H_2O increases strongly with increasing temperature (1,5,8, 12-15). The following equation, fitted by evaluator to the data given by Hagisawa (1), Markant *et al*. (8), Kovachev, Trendafelov and Bakalov (13,14), and Nyvlt *et al*. (15), which are in relatively good agreement, is recommended.

$$\log x = -237.382 + 9474.30/T + 81.8616 \log T \tag{1}$$

with $x = \text{mole fraction of MgSO}_3$, and T = temperature (K). The correlation coefficient is 0.988. The given equation is valid for the range 273 - 363 K. A graph derived from this equation is shown in Fig. 1.

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2. Water; H₂O; [7732-18-5]

EVALUATOR:

H.D. Lutz,

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CRITICAL EVALUATION: (continued)

 $MgSO_3.3H_2O$

Data on the solubility of $MgSO_3.3H_2O$ in water have also been reported by several authors (8,9,13,14,16). The published data are in relatively good agreement.

RECOMMENDED VALUES

The solubility of $MgSO_3$.3 H_2O in water at 323.2 K (50°C) on the molality scale is 0.082 ($^{\pm}0.003$) mol kg^{-1} (8.6 g $MgSO_3/kg$ H_2O).

The solubility of $MgSO_3.3H_2O$ decreases with increasing temperature (1,13,16). The following equation is fitted to the data:

$$\log x = -71.873 + 3811.30/T + 22.8142 \log T \tag{2}$$

This equation is valid for the range 315 - 373 K. The correlation coefficient is 0.997. A graph of this equation is included in Fig. 1.

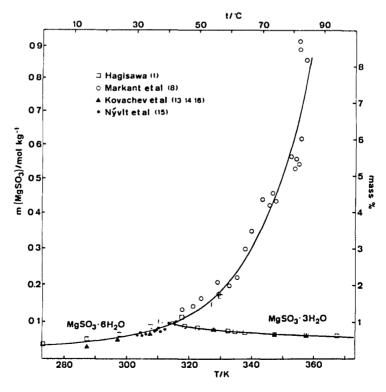


Fig. 1 Solubility of magnesium sulfite in water, as recommended for 273 - 373 K (equations (1) and (2)).

Magnesium sulfite; MgSO₃; [7757-88-2]

2. Water; H₂O; [7732-18-5]

EVALUATOR:

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CRITICAL EVALUATION: (continued)

OTHER HYDRATES

Data on the solubility of other lower hydrates of magnesium sulfite, i.e. $MgSO_3.xH_2O$ and $MgSO_3.xH_2O$, have been reported by Markant *et al.* (8). The temperature coefficient of the solubility of these hydrates has been found to be negative.

SOLUBILITY IN THE SYSTEM MgSO3-SO2-H2O

The solubility of magnesium sulfite increases very strongly with increasing SO_2 content of the solution (1,8,10-12,17-20). The reported numerical data are in relatively good agreement. The following equation, fitted (by evaluator) to the values given by Hagisawa (1), Yakimets et al. (11), and Conrad et al. (17), is recommended for the solubility of MgSO₃.6H₂O in aqueous sulfurous acid solutions at 298.2 K (molality scale)

$$m(MgSO_3) = 0.0347 + 0.4995 m(SO_2 tot).$$
 (3)

The correlation coefficient is 0.99988. A graph derived from this equation is shown in Fig. 2.

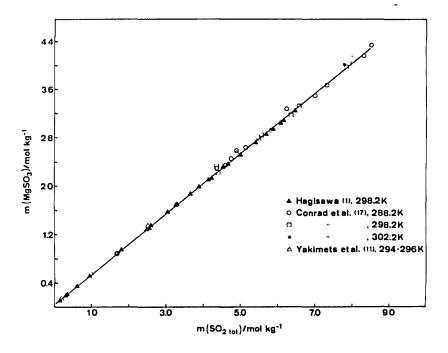


Fig. 2 Solubility of magnesium sulfite, $MgSO_3.6H_2O$, in aqueous sulfurous acid solutions, as recommended for 298 K (equation (3)).

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2. Water; H₂O; [7732-18-5]

EVALUATOR:

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CRITICAL EVALUATION: (continued)

Studies on the partial pressure of SO_2 over saturated solutions of magnesium sulfite are scarce (1,17,20). The data given by Hagisawa (1) for 298 K are recommended (see Fig. 3). The following equation is fitted (by evaluator) to these data:

$$\log m(MgSO_3) = -0.66763 + 0.26370 \log p(SO_2)$$
 (4)

The correlation coefficient is 0.9977.

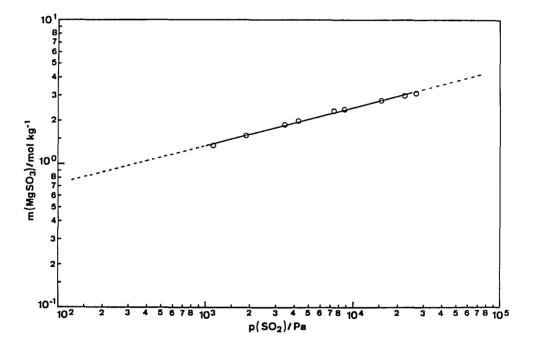


Fig. 3 Solubility of magnesium sulfite, $MgSO_3.6H_2O$, in aqueous sulfurous acid solutions vs. partial pressure of sulfur dioxide at 298 K (1) (equation (4)).

Numerical data on the solubility of magnesium sulfite in aqueous sulfurous acid solutions above ambient temperature are reported by Markant et al. (8), Pinaev (12), Conrad et al. (17), and Semishin et al. (19), viz. for 308 - 338 K; 313.2 K, 323.2 K, 333.2 K (12); 308.2 K (17); 308.2 - 343.2 K (19). For temperatures above 313 K, however, the nature of the solid phase (e.g. $MgSO_3.3H_2O$ or other lower hydrates) present in the saturated solution has not been specified by most authors. The data indicate that the temperature dependence of the solubility of magnesium sulfite is relatively small in the presence of large amounts of free SO_2 .

- 1. Magnesium sulfite; MgSO₃; [7757-88-2]
- 2. Water; H₂O; [7732-18-5]

EVALUATOR:

H.D. Lutz, Dept. of Chemistry, University of Siegen, FR Germany. January 1985.

CRITICAL EVALUATION: (continued)

SOLUBILITY OF MAGNESIUM SULFITE IN THE PRESENCE OF MgSO4, MgCl2, Na2SO3, AND SUCROSE

The solubility of magnesium sulfite in water is strongly affected by the presence of a third component. Numerical data are reported for the systems $MgSO_3-MgSO_4-H_2O$ (12,13,15), $MgSO_3-MgSO_4-SO_2-H_2O$ (19,20), $MgSO_3-MgC1-H_2O$ (16), $MgSO_3-MgC1_2-SO_2-H_2O$ (21), $MgSO_3-Na_2SO_3-H_2O$ (14), and $MgSO_3-sucrose-H_2O$ (22).

In the system $MgSO_3-MgSO_4-H_2O$ the solubilities of both $MgSO_3.6H_2O$ and $MgSO_3.3H_2O$ at first increase with increasing $MgSO_4$ content (12,13,15) of up to $m(MgSO_4) = 1.5 - 2.5$ mol kg^{-1} (10 - 20 mass %) to approximately twice the amount soluble in pure water and then decrease up to saturation with $MgSO_4$ (12,13). This behaviour has been observed for all temperatures investigated, viz. 288 K (13), 306.8 - 314.3 K (15), 308 K (13), 313.2 K (12), 323.2 K (12), 328 K (13), 333.2 K (12), and 348 K (13), irrespective of the solid phase present, and also in the presence of excess of sulfur dioxide (19,20). Graphs drawn (by evaluator) from data reported by Kovachev et al. (13) are shown in Fig. 4.

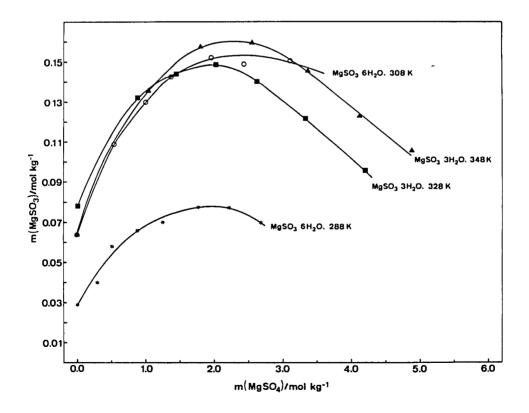


Fig. 4 Solubility of magnesium sulfite in aqueous magnesium sulfate solutions (13).

- 1. Magnesium sulfite; MgSO₃; [7757-88-2]
- 2. Water; H₂O; [7732-18-5]

EVALUATOR:

H.D. Lutz, Dept. of Chemistry, University of Siegen, FR Germany. January 1985.

CRITICAL EVALUATION: (continued)

Numerical data on the solubility of $MgSO_3.3H_2O$ in the presence of magnesium chloride are given by Bakalov et a1. (16) and McIlroy (21). Bakalov's data (16) indicate that the solubility of magnesium sulfite, i.e. $MgSO_3.3H_2O$, decreases to 20 and 30% of the amount soluble in pure water at a $MgCl_2$ concentration of approximately 40 mass % at 348 K and 358 K, respectively.

In the system $MgSO_3-Na_2SO_2-H_2O$ the solubilities of both $MgSO_3.6H_2O$ and $MgSO_3.3H_2O$ at first increase with increasing Na_2SO_3 content (at 298.2 K to approximately four times the amount soluble in pure water). At higher concentrations of Na_2SO_3 , i.e. higher than 10 mass %, the solubility of magnesium sulfite decreases to values less than the solubility in pure water.

The solid phases at high ${\rm Na_2SO_3}$ concentrations are hydrates of ternary sodium magnesium sulfites of not exactly known composition.

The solubility of magnesium sulfite is not much affected by the presence of sucrose (22) in the solution.

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- 2. Water; H₂O; [7732-18-5]

EVALUATOR:

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CRITICAL EVALUATION: (continued)

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